



Supercritical fluid extraction and on-line hydrodechlorination of chlorinated biphenyls catalyzed by polymer-stabilized palladium nanoparticles

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ABSTRACT

Polychlorinated biphenyls spiked in soil can be extracted by a continuous flow supercritical fluid carbon dioxide system and converted on-line to bicyclohexyl using a polymer-stabilized palladium nanoparticle catalyst. The catalytic hydrodechlorination of 4-chlorobiphenyl to biphenyl follows a pseudo-first-order reaction kinetics. The subsequent hydrogenation of biphenyl to bicyclohexyl involves two steps with cyclohexylbenzene as an intermediate. The hydrogenation reactions also follow pseudo-first-order kinetics and the rate constants are given in this paper.

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1. Introduction

Polychlorinated biphenyls (PCBs), due to their thermal and chemical stability, were widely used prior to 1970s for a range of applications including dielectric fluids, heat transfer fluids, lubricating oil, etc. After decades of use, PCBs were found having potential toxicity to human health. Two major PCB poisoning incidents occurred in Japan in 1968 and in Taiwan in 1979, known as the “Yusho” incident and the “Yu-Cheng” incident, respectively. Thousands of people were affected with serious health problems caused by ingestion of PCB-contaminated oil [1,2]. Due to inappropriate use and illegal disposal in the pre-1970 era, large quantities of PCBs were released into the environment and accumulated in soil and sediments causing serious environmental concerns. In 1972, the use of PCBs was prohibited in Japan by strict regulations. Nevertheless, the remediation of existing PCBs and PCB-contaminated soils are big environmental issues remain unsolved.

The remediation of PCB-contaminated soil usually involves two steps, extraction followed by destruction of PCBs. Conventionally, PCBs are removed from soil by organic solvent extraction such as Soxhlet and Soxtec extractions prior to destruction [3]. However, the process is time-consuming and generates large amounts of organic liquid wastes. Supercritical fluid carbon dioxide (SF-CO₂),

because of its chemical inertness, non-flammable nature, and mild critical constants ($P_c = 72.8$ atm and $T_c = 31.1$ °C), is a good alternative for replacing conventional organic solvents. Moreover, the high diffusivity and low viscosity of SF-CO₂ tend to enhance the mass transfer and penetration ability of the fluid, resulting in high extraction efficiencies for solid substances. It is known that PCBs dissolve in SF-CO₂ [4,5] and the solubility varies with the pressure and temperature of the fluid phase. Chiu et al. performed supercritical fluid extraction (SFE) of 2,2',6,6'-tetrachlorobiphenyl (BZ#54) from sand and soil [6]. The extraction efficiencies of BZ#54 in sand and in soil are 97% and 60%, respectively, at 200 atm of CO₂ and 100 °C with 0.5 h each of static and dynamic extraction. When increasing temperature to 150 °C, nearly 100% extraction of the PCBs can be achieved indicating that higher temperature will enhance the supercritical fluid extraction efficiency of PCBs from soil [7].

Currently, a number of techniques including thermal, chemical, and biochemical methods are capable of destroying PCBs. Incineration and oxidation are two of the widely used methods [8]. However, the high energy requirement and the possibility of producing toxic byproducts such as dioxin by these methods are problems of concern. Bio-remediation is a green method but the relatively slow reaction rates may limit its application [9]. In contrast, reduction is a cleaner and more efficient way for the destruction of PCBs, especially for the PCB congeners with higher chlorine numbers. Catalytic hydrodechlorination (HDC), among various reduction methods, draws most attention because of its effectiveness [10–12]. Catalytic HDC of PCBs is usually done in an

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organic solvent with different heterogeneous catalysts, including commercially available carbon-based palladium catalyst (Pd/C). Again, the process generates organic wastes and dispersion of the catalyst in a heterogeneous catalysis system is not easy to achieve. In addition, the solubility of H₂ in organic solvents is generally low which may limit the efficiency of conventional HDC. In our previous study, these disadvantages were overcome by replacing organic solvents with SF-CO₂ combined with polymer-stabilized metal nano-catalysts [13,14]. The reason of using polymer-stabilized metal nano-catalysts in SF-CO₂ is based on the fact that polymers often swell in SF-CO₂ [15]. Thus, PCBs dissolved in SF-CO₂ can diffuse into the polymer structure contacting all metal nanoparticles dispersed in the polymer for catalytic reactions. Using a high density polyethylene stabilized Pd nanoparticles as catalysts, some PCBs were effectively converted to bicyclohexyl in SF-CO₂ at 100 atm and 100 °C in 1 h. The catalytic ability of the polymer-stabilized Pd nano-catalysts remains constant after repeated use probably due to the self-cleaning nature of SF-CO₂.

Recently, SF-CO₂ extraction coupled with supercritical water oxidation (SCWO) for remediation of PCB-contaminated soil has been reported and the cost of this method has also been evaluated [16]. Compared with other cleanup methods for PCB-contaminated soil such as solvent extraction or incineration, this approach is efficient and economic according to the report. However, the coupling between SF-CO₂ and SCWO and the harsh critical condition of SCWO ($P_c = 218.3$ atm and $T_c = 374.2$ °C) may create safety problems for the operation. Herein we report the feasibility of using a continuous flow SFE process coupled with on-line catalytic HDC of PCBs with a polymer-stabilized Pd nanoparticle catalyst. The approach offers several advantages. First, the construction of experimental setup is relative simple and the experimental conditions are mild. Second, the approach has no depressurization step between extraction and destruction. Third, the process allows continuous extraction and hydrodechlorination of PCBs which simplifies the remediation procedure and minimizes the solubility problem usually encountered in the static mode. Poliakoff et al. has performed continuous chemical reactions of organic compounds in supercritical fluids and extended some systems to industrial scale operations [17–21].

The selectivity of a catalytic hydrogenation reaction in SF-CO₂ may be controlled by experimental conditions including temperature, pressure, H₂ concentration, and the loading and nature of the catalyst. In this study, a monochlorinated biphenyl was first used as an example to demonstrate the feasibility of our approach and to evaluate the effect of CO₂ flow rate on the extraction of the chlorobiphenyl, on-line hydrodechlorination efficiency, and collection of the final products at the end. In addition, a kinetic study of the catalytic HDC of the monochlorinated biphenyl in SF-CO₂ via in situ UV/vis spectroscopic measurements was performed to elucidate the dynamic mode data. Finally, the remediation of an artificially prepared PCB-contaminated soil was performed using the conditions determined from the monochlorinated biphenyl system.

2. Experimental

2.1. Chemicals and reagents

Palladium hexafluoroacetylacetonate [Pd(hfa)₂] (97%), high density polyethylene (HDPE) beads (circular flat white beads with average diameter, height, and weight of about 3 mm, 1.5 mm, and 14 mg, respectively), biphenyl, cyclohexylbenzene, bicyclohexyl, 4-bromobiphenyl (as a GC/MS internal standard), and sea sand were purchased from Aldrich (Milwaukee, WI). Liquid carbon dioxide (99.99%) and hydrogen gas were supplied by Oxarc

(Spokane, WA). 4-chlorobiphenyl (BZ#3) and Aroclor 1254 were purchased from Ultra Scientific (North Kingstown, RI). HPLC grade hexane used as a trap solution was purchased from Fisher Scientific (Fair Lawn, NJ). A native Idaho soil was collected in the vicinity of the University of Idaho.

2.2. Catalyst and sample preparation

The synthesis of Pd/HDPE catalysts was described in a previous paper [14]. Typically, Pd(hfa)₂ was impregnated into HDPE beads in a stainless steel cell pressurized by SF-CO₂ at 90 °C and 100 atm pressure for 3 h. After impregnation, Pd²⁺ in Pd(hfa)₂ was reduced to zero-valent Pd by hydrogen gas and formed nanoparticles in the HDPE beads. The beads were then cleaned by neat SF-CO₂ to remove impurities. TEM (transmission electron microscope) pictures show the size distribution of Pd nanoparticles embedded in HDPE beads is in the range of 2–10 nm with an average value of 5 nm and they are primarily in the zero-valence state according to the XPS (X-ray photon spectroscopy) data. The Pd concentration of the beads based on neutron activation analysis (NAA) is about 430 ppm [14]. Sea sand was used without further treatment. The soil was air-dried, ground and passed through a 2 mm sieve. The preparation of PCB-contaminated soil is described as follows. Typically, 1 mg of BZ#3 (5.28×10^{-6} mol) or Aroclor 1254 (about 3.02×10^{-6} mol) dissolved in 100 μ L of hexane was spiked in 1000 mg of sea sand or soil. After evaporation of hexane, the PCB-spiked sample was ready for experiments. The internal standard stock solution was prepared by dissolving 18.5 mg of 4-bromobiphenyl in 3 mL of hexane. 10 μ L of the stock solution containing 2.63×10^{-7} mol of 4-bromobiphenyl was added to each sample for GC/MS analysis. For in situ UV/vis spectroscopic measurement in SF-CO₂, 1.5×10^{-2} M of BZ#3, 7.3×10^{-2} M of biphenyl, and 7.5×10^{-2} M of cyclohexylbenzene in hexane were prepared as stock solutions.

2.3. Instruments

2.3.1. SFE and catalytic HDC of PCBs

The experimental setup is shown in Fig. 1. The liquid CO₂ was metered and pressurized by an ISCO syringe pump (Model 260D, Lincoln, NB) with a series D pump controller. Cell 1 is a 60 mL cylindrical stainless steel cell for H₂ storage. Cell 2 is a 6.9 mL stainless steel extraction cell where PCB-spiked matrix is placed. Both ends of Cell 2 have filters to prevent the solid sample from flowing out of the cell that may block the system. Cell 3 is a 10 mL reaction cell (20 cm in length with an inside diameter of 0.8 cm) purchased from High Pressure Equipment Company (HiP, Erie, PA). The cell is filled with Pd/HDPE beads (about 5.4 g). All valves are HiP Taper Seal needle valves for 1/16 and 1/8 in. o.d. tubings. A 25 mL glass cylinder tube with 10 mL hexane was used at the end of the system for trapping the products and unreacted PCBs. Temperature was controlled by a Varian GC oven (Model 3700, Palo Alto, CA). The products were analyzed by GC/MS (Model HP-6890 series and JOEL JMS AX-505HA) with a DB-5 column (0.23 mm i.d. and 0.25 μ m film thickness). The GC/MS condition was: 1 μ L splitless injection at 250 °C, initial temperature 55 °C for 4 min and final temperature 280 °C with a rate of 8 °C/min.

2.3.2. Kinetic study in SF-CO₂ via in situ UV/vis spectroscopic measurement

The apparatus for the kinetic study is shown in Fig. 2. Cell 1 is a 20 mL CO₂/H₂ mixing chamber. Cell 2 is a 20 mL high-pressure reactor connected to a UV/vis spectrometer with a charge-coupled device (CCD) array via optical fibers (Model 440, Spectral Instruments, Inc., Tucson, AZ). The detail information of the

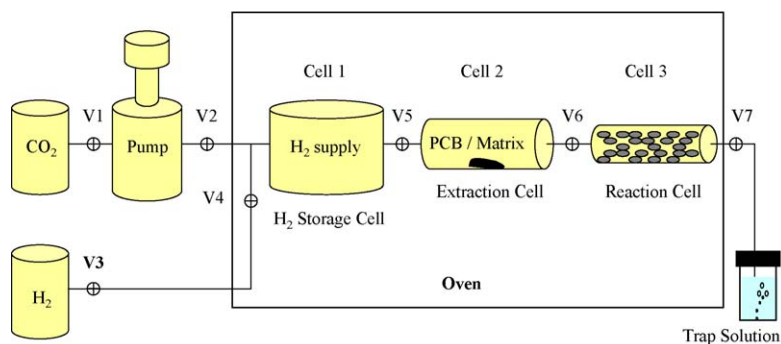


Fig. 1. Apparatus for continuous SFE coupled with on-line Pd/HDPE-catalyzed HDC of PCB. Cell 1 is a 60 mL H₂ storage cell. Cell 2 is a 6.9 mL extraction cell where the PCB-spiked sample is placed. Cell 3 is a 10 mL reaction cell filled with Pd/HDPE beads. 10 mL hexane in a 25 mL cylinder tube is used as the trap solvent.

high-pressure fiber-optic cell is given in the literature [22]. Temperature was controlled by a Varian GC oven and a heating bag connected to a variable autotransformer (Staco energy products Co. Dayton, OH). Pressure and temperature inside the fiber-optic cell were monitored by a pressure gauge (Omega Engineering, Inc.) and a thermometer (Model HH23, KMTSS-062U-6 thermocouple, Omega), respectively.

2.4. Experimental procedure

2.4.1. SFE and catalytic HDC of PCBs

The experimental procedure for SFE of BZ#3 and the on-line HDC is given as follows: (1) place PCB-spiked matrix in Cell 2 and fully fill Cell 3 with Pd/HDPE beads. (2) Purge the system with 10 atm of H₂ with Valve 2 closed and increase temperature to 100 °C. (3) After Step 2, pressurize the system with CO₂ to 200 atm with Valve 2 open and Valve 4 and 7 closed. (4) When the system is stable, slightly open Valve 7. (5) Run the process for 1 h with a fixed flow rate of CO₂ and collect products in 10 mL hexane. Addition of extra hexane during experiments is necessary to keep enough hexane in the collection vial. The flow rate is displayed on the screen of the ISCO pump controller and is controlled by Valve 7. (6) At the end of 1 h, close Valve 7 and remove the trap solution. Two millilitres of the 10 mL trap solution mixed with 10 µL of the internal standard is analyzed by GC/MS to determine conversion, selectivity, and collection efficiency. (7) Depressurize the system with Valve 2 closed and Valve 7 open. (8) After depressurization, wash Cell 2 and the solid sample with 4 mL hexane and transfer the resulting mixture to a 4 mL vial.

The solution is then shaken for 1 h by a wrist-action shaker. After that, pipette 2 mL of the hexane out and mixed with 10 µL of the internal standard for GC/MS analysis to determine the extraction efficiency. (9) Clean the system with SF-CO₂ at 200 atm of CO₂ (containing 10 atm of H₂) at 100 °C for 1 h to remove PCB residue and remaining products from the system. The terms used in expressing the extraction and conversion results are defined as follows: extraction efficiency = [(original PCB – PCB left in Cell 2)/(original PCB)] × 100%, collection efficiency = [(PCB and products in trap solution)/(original PCB)] × 100%, percent conversion = [(products)/(products plus PCB in trap solution)] × 100%, and selectivity = [(one specific product)/(all products)] × 100%.

2.4.2. Kinetic study of HDC via in situ spectroscopic measurements

The procedure for kinetic study of HDC of BZ#3 is given as follows: (1) fill half of Cell 2 with Pd/HDPE beads. (2) The system is preheated to a designated temperature. (3) 50 µL of the BZ#3 stock solution is added into a 0.5 mL glass cup and air-dried to remove hexane. The cup is then placed on top of the Pd/HDPE beads in Cell 2. (4) Pressurize Cell 2 with CO₂ to 100 atm with Valve 2 and 7 open and the rest of the valves closed. (5) Close Valve 2 and 7 and open Valve 8 to release CO₂ in the connecting tubing. (6) Close Valve 8 and open Valve 3, 4, and 5 and fill Cell 1 with 10 atm of H₂. (7) Close Valve 3 and 4 and open Valve 2 to pressurize Cell 1 with CO₂ to 200 atm. (8) Introduce 200 atm of CO₂/H₂ mixture to Cell 2 by opening Valve 6 due to pressure difference. (9) Turn on the spectrometer and record UV/vis spectra every 30 s. (10) After each experiment, clean the system with at least 30 mL of CO₂ with 1.0 mL/min of flow rate.

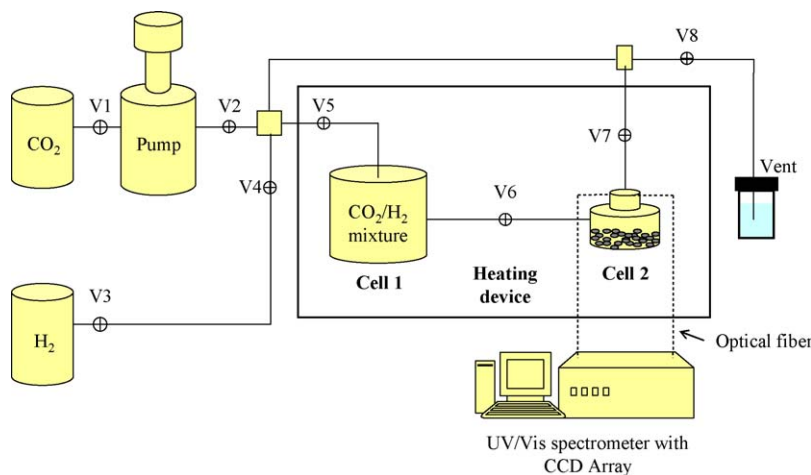


Fig. 2. Apparatus for kinetic study of catalytic HDC of BZ#3 in SF-CO₂ via in situ UV/vis spectroscopic measurements. Cell 1 is a 20 mL CO₂/H₂ mixture cell. Cell 2 is a 20 mL high-pressure reactor connected to a UV/vis spectrometer with CCD array via optical fibers.

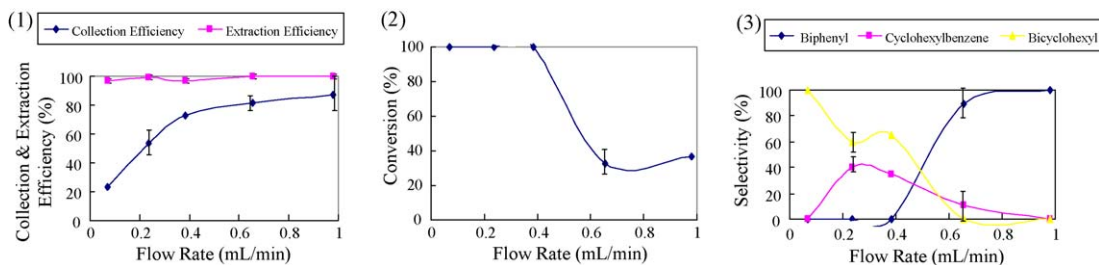


Fig. 3. Continuous SFE coupled with on-line Pd/HDPE-catalyzed HDC of BZ#3. (1) Collection efficiency and extraction efficiency versus flow rate, (2) Conversion versus flow rate, (3) Selectivity versus flow rate. Conditions: 1 mg of BZ#3, 1000 mg of sea sand, 200 atm of CO₂, 10 atm of H₂, 100 °C, and 1 h.

3. Results and discussion

3.1. SFE and catalytic HDC of BZ#3 in sand

One gram of sea sand spiked with BZ#3 (1 mg or 1000 ppm) was used in each experiment. The CO₂ pressure and temperature were set at 200 atm and 100 °C for both the SFE and the hydrogenation reaction with a H₂ partial pressure of 10 atm in the latter step. According to the literature, a minimum of 100 °C is required for effective extraction of PCBs from soil by SF-CO₂ [6]. Our previous study indicates that conversion of BZ#3 to bicyclohexyl increases with temperature using this HDC technique [14]. However, further raise in temperature could result in melting of the HDPE catalyst which occurs around 120 °C. Therefore, a temperature of 100 °C appears to be a good choice for this hyphenated SFE of PCBs and on-line HDC study. The solubility of PCBs in SF-CO₂ is known to increase slightly with pressure at a given temperature [4]. However, at a relatively high-pressure (e.g. >300 atm) leakage of the reaction system could be a problem for routine SF-CO₂ operations. For these reasons, several previous HDC studies in SF-CO₂ were conducted at a pressure of 200 atm [4,26]. For the present study, we also chose 200 atm for the SFE and on-line HDC of PCBs in our experiments.

The extraction efficiency of BZ#3 from the sea sand and its collection efficiency in the trap solution under the specified experimental conditions and at different flow rates are given in Fig. 3(1). The extraction efficiency of each trial obtained by analyzing the amount of BZ#3 remaining in the sand is nearly 100% in the flow rate range shown in the figure. The collection efficiency is 30% at about 0.1 mL/min and increases with flow rate reaching 88% at 1.0 mL/min for a time of 60 min. The result indicates that BZ#3 is nearly 100% extracted from sea sand in Cell 2 and carried by SF-CO₂ to Cell 3 which is designed for catalytic hydrogenation reactions. At a low flow rate, the monochlorobiphenyl seems to remain in the system probably on the walls of Cell 3 or the connectors and tubing of the supercritical fluid extraction system. At a high flow rate, the extracted BZ#3 is more effectively carried out of the system by SF-CO₂ and trapped in hexane.

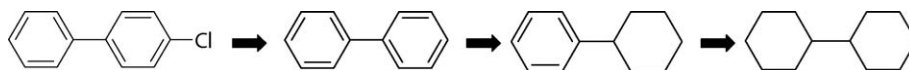
The catalytic hydrogenation of BZ#3 may involve several steps including hydrodechlorination of BZ#3 to biphenyl, hydrogenation of biphenyl to cyclohexylbenzene and finally to bicyclohexyl as shown in Scheme 1. The variation of the efficiency of catalytic hydrodechlorination of BZ#3 in supercritical CO₂ (at 200 atm and 100 °C) with respect to the flow rate is shown in Fig. 3(2). Slower flow rates tend to increase the conversion efficiency due to longer contact times in the reactor. The monochlorobiphenyl was 100% converted below 0.4 mL/min. When the flow rate is above 0.4 mL/

min, BZ#3 starts to appear and the percent conversion continues to decrease with further increase in flow rate. The result indicates that for complete hydrodechlorination of BZ#3, the flow rate must be lower than 0.4 mL/min under our experimental conditions.

The distribution of products from the catalytic hydrogenation of BZ#3 at different supercritical fluid flow rates is given in Fig. 3(3). At low flow rates (below 0.1 mL/min), BZ#3 is nearly 100% converted to bicyclohexyl. Above 0.1 mL/min, bicyclohexyl begins to decrease and cyclohexylbenzene starts to appear. Above 0.4 mL/min, biphenyl starts to appear and increases with the flow rate while cyclohexylbenzene and bicyclohexyl decreased with the increase in flow rate. Above 0.8 mL/min, biphenyl is the only product detected in the trap solution. The result indicates that at a low flow rate (0.1 mL/min), BZ#3 undergoes complete HDC and hydrogenation of biphenyl to bicyclohexyl is virtually complete. The only product under these conditions is the benign bicyclohexyl. As the flow rate increases, the catalytic hydrogenation reaction of BZ#3 is only partially complete. Above 0.4 mL/min, bicyclohexyl, cyclohexylbenzene and biphenyl are all present in the system accompanying the unreacted BZ#3.

From the above experimental data and discussion, we conclude that BZ#3 can be successfully extracted from matrix in Cell 2 and transported to Cell 3 for catalytic reactions in a continuous flow system. The flow rate can affect the degree of the catalytic reactions and the collection efficiency of the end products at a fixed experimental time. At low flow rates, the residence time is long allowing BZ#3 to undergo complete HDC to biphenyl and then to bicyclohexyl. However, the collection efficiency is low at 0.1 mL/min suggesting that most of the products still remain in the system due to the low CO₂ volume passing through the system in a fixed experimental time. At high flow rates, the collection efficiency is improved because a larger volume of CO₂ is used in a fixed time but incomplete catalytic reactions occur. Increasing volume of the reaction cell can increase the residence time but would result in higher costs because an excess amount of the catalyst is required to fill the reaction cell. Therefore, choosing a suitable flow rate in this dynamic supercritical fluid system for extraction and hydrodechlorination of PCBs that gives satisfying collection efficiency and yet results in benign bicyclic compounds is important for remediation applications.

By combination of Fig. 3(2) and (3) and converting the x-axis unit from flow rate to residence time based on the assumption that PCBs flow linearly through the free volume of the reactor, the resulting plot is shown in Fig. 4. According to Fig. 4, the reaction rates of BZ#3 to biphenyl and from biphenyl to cyclohexylbenzene are similar and are both faster than the conversion of cyclohexylbenzene to bicyclohexyl.



Scheme 1. Hydrodechlorination of BZ#3 and subsequent hydrogenation of biphenyl to bicyclohexyl.

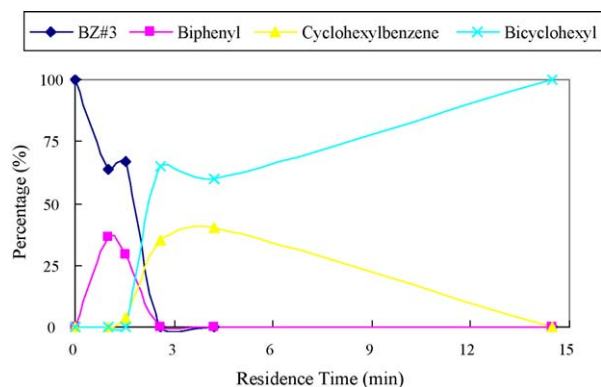


Fig. 4. Product distribution versus residence time for on-line Pd/HDPE-catalyzed HDC of BZ#3.

3.2. Kinetic study of catalytic HDC of BZ#3 in SF-CO₂

The UV/vis spectrum of BZ#3, biphenyl, and cyclohexylbenzene in SF-CO₂ are shown in Fig. 5(1–3), respectively. Bicyclohexyl shows no characteristic absorption peak in the UV/vis region. The characteristic absorption peaks of BZ#3 (249 nm), biphenyl (243 nm) and cyclohexylbenzene (207 nm) can be used to monitor their concentrations in the SF-CO₂ phase during the catalytic hydrogenation processes to evaluate their reaction kinetics. About 7.5×10^{-7} mol of BZ#3 was used in each HDC kinetic experiment. The CO₂ pressure and temperature were set at 200 atm and 50 °C with a H₂ partial pressure of 10 atm for the kinetic experiments. Because the reaction vessel is connected to a large reservoir with 10 atm of H₂ and 190 atm of CO₂, the partial pressure of H₂ in the reaction system was near constant and in large excess relative to the reactant BZ#3. The decrease of BZ#3 in the reaction cell with respect to time was monitored by the fiber-optic spectrometer as shown in Fig. 6(1). The amount of BZ#3 in the SF-CO₂ phase appeared to decrease exponentially with time in this system under the specified experimental conditions. A plot of $\ln[A/A_0]$ versus time yields a straight line as shown in Fig. 6(2) suggesting the

catalytic hydrodechlorination follows a pseudo-first-order reaction kinetics. The rate constant k calculated from the slope of the straight line is about 0.0794 min^{-1} according to the data given in Fig. 6(2). The half-life of the hydrodechlorination reaction is 8.73 min.

Several recent studies of HDC of PCBs catalyzed by NiMo/ γ -Al₂O₃ showed pseudo-first-order kinetics at a fixed H₂ pressure and low PCB concentrations [24,25]. Schioppa et al. evaluated the mass transfer resistance in their system at 300 °C and a hydrogen pressure of 20 bar with two different sizes (0.1 mm and 3–4.5 mm diameter) of the NiMo catalyst [25]. According to their report, the external mass transfer is absent for both sizes. However, the internal mass transfer resistance exists for the larger size catalyst and diffusion in the catalyst porosity plays a significant role. The diffusion coefficient of 2-chlorobiphenyl in the NiMo catalyst in hexadecane was estimated to be $3.28 \times 10^{-5} \text{ cm}^2/\text{s}$ at 300 °C and 20 bars of hydrogen pressure. Diffusion of PCBs in HDPE under SF-CO₂ atmosphere has not been reported. The diffusion coefficient of CO₂ in molten HDPE is about $9 \times 10^{-5} \text{ cm}^2/\text{s}$ at 200 °C and 120 atm [27]. It appears that the diffusion coefficient of 2-chlorobiphenyl in HDPE under our SF-CO₂ conditions (100 °C) should be much lower than $9 \times 10^{-5} \text{ cm}^2/\text{s}$ and smaller than the value of PCBs in the NiMo catalyst reported by Schioppa et al. [25]. In addition, Marshall et al. have studied hydrogenation of benzo[a]pyrene catalyzed by a Pd/HDPE catalyst in SF-CO₂ [26]. They pointed out that by reducing the diameter of the Pd/HDPE catalyst from 2 mm to 1 mm while keeping other parameters constant, the conversion increased from 26% to 43% indicating the existence of internal mass transfer resistance in the Pd/HDPE catalyst. Based on the literature information, we think that diffusion probably also plays a major role in our observed kinetic constant similar to that reported for the HDC of PCBs catalyzed by the NiMo catalyst [25].

The catalytic hydrogenation of biphenyl to bicyclohexyl in this system is studied separately using biphenyl or cyclohexylbenzene as the starting material under the same experimental conditions. The hydrogenation of biphenyl to cyclohexylbenzene and then to bicyclohexyl as shown in Scheme 1 is a consecutive reaction of the type $A \rightarrow B \rightarrow C$. The decrease of biphenyl in this system also

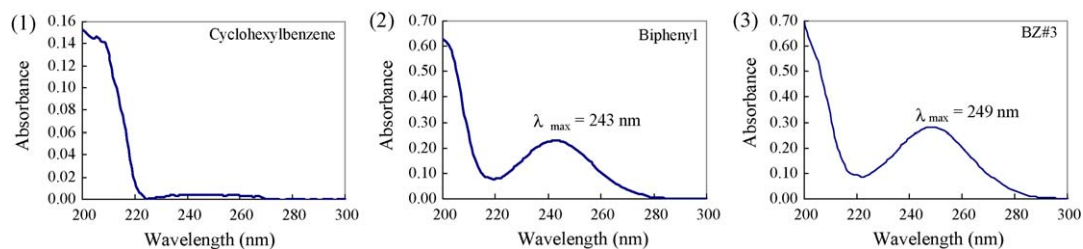


Fig. 5. UV/vis spectrum of (1) cyclohexylbenzene, (2) biphenyl, and (3) BZ#3 in SF-CO₂.

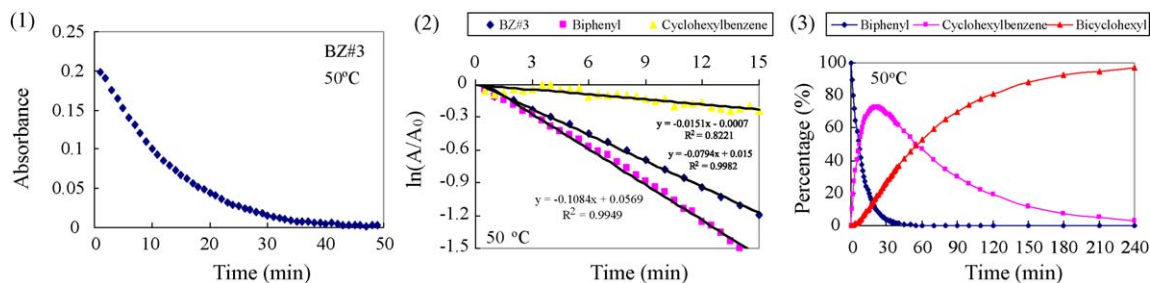


Fig. 6. Kinetic study in SF-CO₂ via in situ UV/vis spectroscopic measurement. (1) A plot of BZ#3 absorbance versus time. (2) A plot of $\ln(A/A_0)$ versus time for HDC of BZ#3 and hydrogenation of biphenyl and cyclohexylbenzene. (3) A product distribution versus time plot for hydrogenation of biphenyl based on experimentally-obtained rate constants. Condition: $\sim 7.5 \times 10^{-7}$ mol of reactants, 200 atm of CO₂, 10 atm of H₂, 50 °C, and static mode.

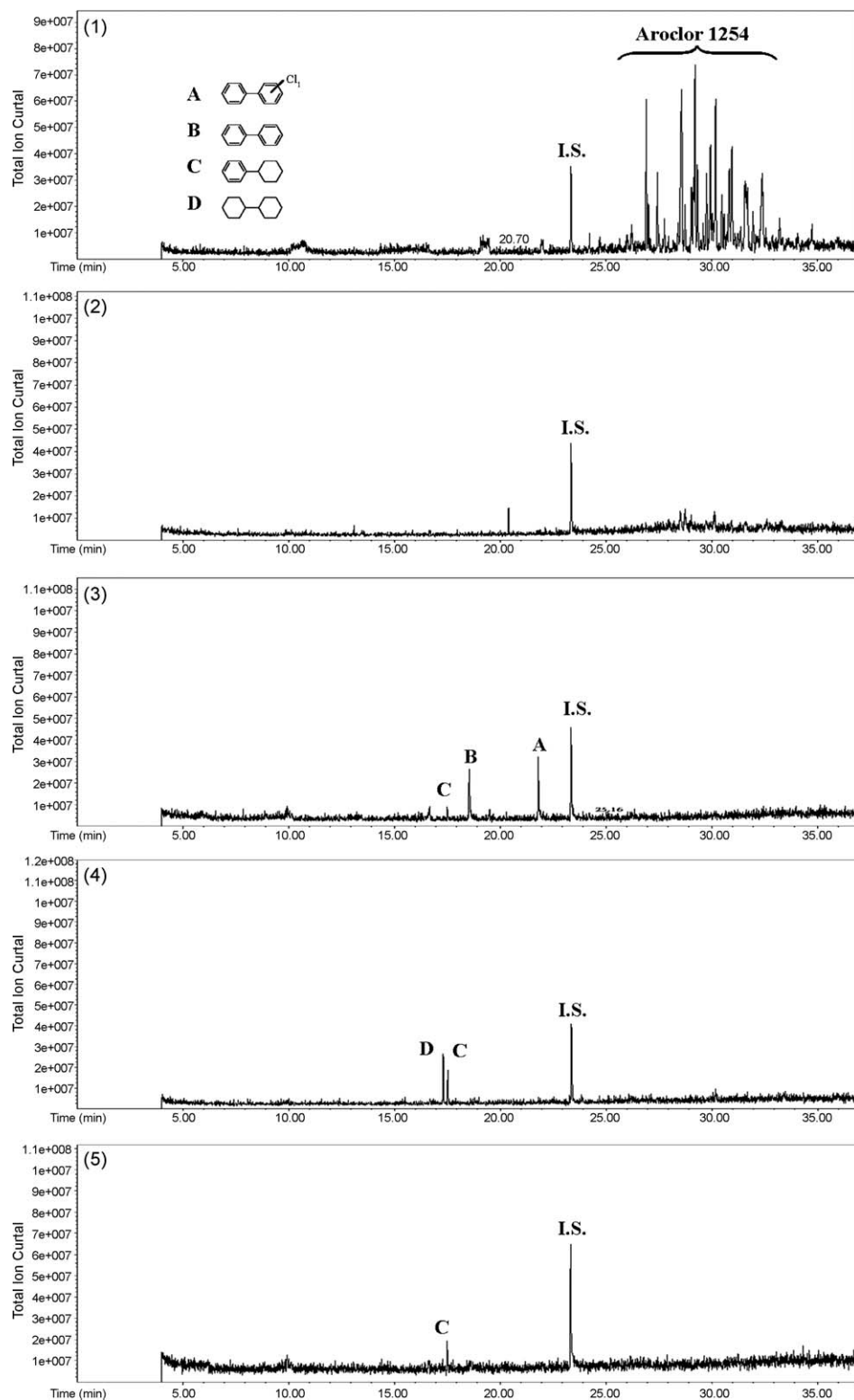


Fig. 7. GC/MS chromatograms. (1) Standard Aroclor 1254. (2) The wash solution of 0.510 mL/min trial. Extraction efficiency: ~100%. (3) The trap solution of 0.510 mL/min trial. Selectivity: 39% to A, 42% to B, and 19% to C. Collection efficiency: 75%. (4) The trap solution of 0.264 mL/min trial. Selectivity: 40% to C and 60% to D. Collection efficiency: 57%. (5) The trap solution of 15 mL reaction cell trial. Selectivity: 100% to C. Collection efficiency: 28%. Condition: 1 mg of Aroclor 1254, 1000 mg of native soil, 200 atm of CO₂, 10 atm of H₂, 100 °C, and 1 h.

follows a pseudo-first-order reaction as shown in Fig. 6(2) with a rate constant of 0.108 min⁻¹. The observation is consistent with the literature report in which GC/FID was used as the post-analysis method [23]. The hydrogenation of cyclohexylbenzene to bicy-

clohexyl shown in Fig. 6(2) also follows pseudo-first-order kinetics with a *k* value of 0.015 min⁻¹. By fitting the experimental rate constants into the consecutive first-order reaction equations, the variation of biphenyl and cyclohexylbenzene with time in this

system shown in Fig. 6(3) are consistent with the known equations involving two reaction steps $A \rightarrow B \rightarrow C$.

From the calculated rate constants, the reaction rates of BZ#3 to biphenyl and biphenyl to cyclohexylbenzene are similar and faster than that of cyclohexylbenzene to bicyclohexyl, which is consistent with the dynamic data shown in Fig. 4.

3.3. SFE and catalytic HDC of Aroclor 1254 in soil

A native Idaho soil spiked with 1000 ppm Aroclor 1254, a PCB mixture containing 54% chlorine by mass which corresponds to five chlorine substitutions in biphenyl on average, was studied for its extraction and hydrodechlorination following the conditions obtained from the monochlorobiphenyl study. The chromatogram of the standard Aroclor 1254 is shown in Fig. 7(1). The peaks between 25.0 min and 35.0 min are for Aroclor 1254. The peak at 23.3 min is 4-bromobiphenyl, an internal standard. The peak positions of four possible products are 21.8 min for monochlorinated biphenyl (A), 18.5 min for biphenyl (B), 17.5 min for cyclohexylbenzene (C), and 17.3 min for bicyclohexyl (D).

The first trial of the Aroclor 1254 was performed at 0.510 mL/min of SF-CO₂ flow rate while other parameters remained the same as those described in the previous section, i.e. CO₂ at 100 °C and 200 atm. The chromatogram of the wash solution is shown in Fig. 7(2). The peaks for Aroclor 1254 between 25 min and 35 min almost disappeared indicating that Aroclor 1254 were virtually all extracted from the soil. The chromatogram of the trap solution is shown in Fig. 7(3) and there is no peak for Aroclor 1254 in the chromatogram. Three products were detected and no bicyclohexyl was observed. The selectivity was 39%, 42%, 19%, and 0% for monochlorinated biphenyl, biphenyl, cyclohexylbenzene, and bicyclohexyl, respectively. The result indicates PCBs with high chlorine numbers are all converted to monochlorinated biphenyl. Part of the monochlorinated biphenyl undergoes further catalytic reactions to biphenyl and then to cyclohexylbenzene. The collection efficiency of this trial is 75%.

Several parameters can be varied to improve the conversion of Aroclor 1254 including temperature, flow rate, and the volume of the reactor. Since the melting point of HDPE is around 120 °C and our reaction temperature (100 °C) is close to the m.p. of the polymer, further increase in reaction temperature of the system without damaging the catalyst is limited. The flow rate and the volume of the reaction cell are two parameters easy to control. The chromatogram of the trap solution at a slower flow rate of 0.264 mL/min using the 10 mL reaction cell is shown in Fig. 7(4). No Aroclor 1254 was detected in the trap solution and in the wash solution. Two products were detected with 40% of cyclohexylbenzene and 60% of bicyclohexyl. The collection efficiency of this trial was 57%. The chromatogram of the trap solution with a 15 mL reaction cell is shown in Fig. 7(5). Again, no Aroclor 1254 was detected in the trap solution and the wash solution. The only product was cyclohexylbenzene. The collection efficiency of this trial is 28%. The results of both trials indicate that decreasing flow rate of SF-CO₂ and increasing the reaction cell volume can increase the residence time of PCBs in the reaction cell, which allows more complete catalytic reactions leading to less toxic products. However, these adjustments would require a longer time for collection of the products or more catalyst in the reactor.

The repeatable ability of the Pd/HDPE is also evaluated in the dynamic experiments. No significant decrease in the catalytic activity is observed over 30 dynamic runs. The self-cleaning nature of SF-CO₂ probably has a significant contribution to the repeatable ability of the catalyst.

4. Conclusions

A continuous supercritical fluid extraction process coupled with on-line catalytic hydrodechlorination of PCBs using a polymer-stabilized palladium nanoparticle catalyst is described in this paper. Aroclor 1254 (a PCB mixture with an average of five chlorine substitutions in biphenyl) spiked in a soil can be quantitatively extracted and dechlorinated by the catalyst at 200 atm and 100 °C within 1 h of experimental time. The flow rate of SF-CO₂ affects the collection efficiency, the conversion and selectivity of the catalytic reaction. At a low flow rate of SF-CO₂, complete HDC of PCBs and hydrogenation of biphenyl to bicyclohexyl can be achieved. The optimal SF-CO₂ flow rate probably would vary with the reaction system and should be determined experimentally. This method of destroying PCBs is simple and requires relatively mild conditions compared with other known methods. The hyphenated SFE and on-line HDC technique described in this paper may provide an alternative approach for remediation of PCBs in contaminated soil and may be applied to other chlorinated pollutants as well. A preliminary kinetic study of catalytic HDC of BZ#3 in SF-CO₂ indicates each step of the consecutive reactions is pseudo-first-order and simulation of product distributions versus time can be achieved using the experimental rate constants and the known equations for consecutive first-order reactions.

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